

1st REPORT of the THERMODYNAMICS DISEQUILIBRIUM AND EVOLUTION NAI FOCUS GROUP

Centro de Astrobiología (CSIC-INTA)
Torrejón de Ardoz, Madrid, Spain
March 1-3, 2011



From top to bottom rows:

James Dyke;

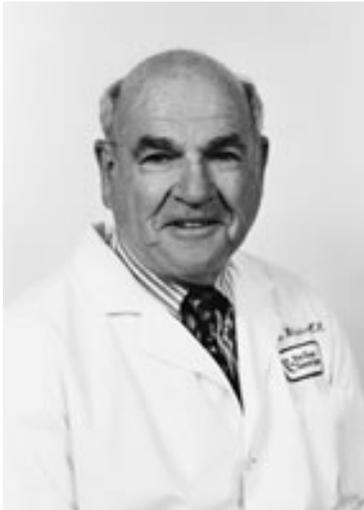
Eugenio Simoncini, Sergio Branciamore, Michael Stich, Francisco López de Saro;

Javier Martin-Torres, Elbert Branscomb, Laurie Barge;

Michael Russell, Sandra Ristori, Alfonso Delgado-Bonal, Jorge Pla, Eva Mateo-Martí, Delphine Nna-Mvondo

Other participants not in the picture: Jesús Martínez-Frías, Federico Morán, Arturo Martín, Gabriel Piedrahita, Manuel de la Torre Juárez, José Cernicharo, and some other CAB members that participated sporadically.

In Memoriam



Dr. **Baruch** S. Blumberg.

Dr. Blumberg was very supportive and showed a great interest in our Focus Group goals. He was felled by an apparent heart attack on April 5, during a meeting at NASA Ames Research Center. He died pursuing his passions: science, exploration, and advancing opportunities for young researchers.

We reflect with gratitude on his leadership as NAI Director from 1999 to 2002, his tireless advocacy for astrobiology and the NAI as well as his support for the TDE Focus Group.

We miss him. Our hearts go out to his family and all those who loved him.

An NAI Central remembrance of Barry has been posted on the NAI website: <http://astrobiology.nasa.gov/articles/nai-central-remembers-barry/>

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ABSTRACTS

Autocatalytic engines, Life, and the Principle of Maximum Entropy Production

Elbert Branscomb

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Physical systems driven sufficiently far from equilibrium by a free energy gradient often undergo an abrupt transformation to a macroscopically organized dynamic structure (an “emergent dissipative structure”; 'EDS') that accelerates the rate at which the driving gradient is dissipated (Kondepudi & Prigogine, 1998, *Modern Thermodynamics*, Wiley). Examples are ubiquitous but include the dissipative flows that give the earth its dynamic geology (e.g. plate tectonics), its interesting weather (e.g. tornadoes) and its encrustment of life. In steady state conditions many EDS's have been found to generate entropy at a rate ('EPR') that appears equal to the maximum rate possible for that gradient given its boundary conditions (its 'MEP' rate); which EPR, importantly, is realized at an intermediate dissipative flow rate and a corresponding intermediate degree of gradient depletion resulting from that flow (Kleidon, 2004, *Clim Change* 66:271-319). For this and other reasons, it has been proposed that such systems, and perhaps all dissipative processes, are governed by a “Maximum Entropy Production Principle” (MEPP) and that this principle may constitute a new law of thermodynamics - arguably subsuming the classical 2nd law (Martyushev & Seleznev, 2006 *Physics Reports*, 426:1–45). The present model-based study attempts to shed light on why the observed MEP behavior of EDS's arises and whether it indicates the operation of a new principle of thermodynamics.

The approach taken exploits the fact that all EDS's are autocatalytic engines (A. Cottrell , 1979, *Contemp. Phys.*, 1-10; A. Lotka, 1924/1956, *Elements of Mathematical Biology*, Ch. XXIV, Dover); that is, they are “free energy converters” (T. Hill, 1989, *Free Energy Transduction and Biochemical Cycle Kinetics*, Springer-Verlag) whose work output (physical or chemical) is 'consumed' by the engine itself to the twin autocatalytic consequences of stabilizing the EDS against decay and 'growing' its free energy processing capacity. However, since the thermodynamic strength of real gradients is reduced by the dissipative flows they induce, if an EDS arises in a gradient it and the gradient form a coupled, dynamic, self-damping system. The present model is constructed to investigate the quantitative implications of this fact.

In particular I explore the behavior of a model based on a heat engine driven by a thermal gradient of finite power in which a fraction of the engine's work is invested in growing its effective conductance and the remainder in reducing its rate of decay. And although the heat engine's free energy conversion is assumed to entail finite internal losses (i.e. to not be 'endoreversible'), the engine is presumed to otherwise operate at maximum output power (Chen, 1994, *J. Phys. D: Appl. Phys.*, 27:1144–1149); that is, and notably in this context, to generate entropy at the *lowest* possible rate given the engine's capacity (Bejan, 1996, *Am. J. Phys.* 64 (8)).

The principle observation about this model's dynamic behavior concerns its asymptotic properties when driven by a sufficient but finite (and stable) energy source. In this circumstance, the system drives engine growth *past* the size it has at the gradient's MEP point. In consequence, the asymptotic EPR is lower than, and the gradient more depleted than, at the MEP point. However, and this is the main conclusion, these asymptotic

deviations from the MEP state are, quite robustly, only fractional and in the case of the EPR are negligible in practical effect. That is, the gradient's MEP point acts to a very close approximation, albeit not exactly, as an attractor for the EDS's growth dynamics with the consequence that this model system behaves sensibly as though it was governed by an MEP principle.

Of course, this result neither reflects nor calls for any new thermodynamic laws or physics. The model's observed MEPP-mimetic behavior is due merely to the 'fortuitous' interaction of several quantitative properties of the model system – although these properties may, it is proposed, also characterize any EDS driven by a finite-power gradient. They are: (1) the dependency of the rate of entropy production on engine capacity falls off very slowly beyond the gradient's MEP point, (2) the thermodynamic force seen by the EDS engine depends non-linearly on the gradient's thermodynamic potential (Chen, *op. cit.*) with the consequence that from the engine's point of view the gradient is already highly depleted at the MEP point, leaving relatively little free energy 'head room' left to drive further growth or support additional maintenance burdens, and (3) as non-equilibrium, inherently unstable states of matter, EDS's require a continuous free energy supply for their maintenance and necessarily have a finite decay rate that is maximal in the absence of one.

The initial part of this work was performed under the auspices of the U.S. Department of Energy by University of California, Lawrence Livermore National Laboratory under Contract W-7405-Eng-48.

Since May, '08 I have enjoyed the help and hospitality of Nigel Goldenfeld and his group in the Institute for Genomic Biology at the University of Illinois.

On the Emergence of Life through “Negative” Entropy Trapping

Michael J. Russell

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Microbes both at the bottom of the evolutionary tree and the base of the food chain hydrogenate carbon dioxide. Four billion years ago our water-world could do the same (as it does still)—abiotically generating methane like an inorganic methanogen, though not nearly so quickly. More rapid reduction appears to be life’s *raison d’être*. So how did life begin? We can think of life’s emergence as being, in part, enabled by a series of self-organizing “negative” entropy traps with serpentinization the first “demon”, transferring energy from the mafic crust to open-system convecting ocean water in the form of heat, hydrogen, methane, ammonia as well as hydroxyl and sulfide ions (Martin et al., 2008, *Nature Rev Microbiol*, 6, 806). The initial trap would be set across the inorganic membrane, formed spontaneously at the site of exhalation of the reduced alkaline fluid now differentiated and separated from its mother liquor—the acidulous, phosphate- and ferrous iron-bearing carbonic ocean (Nitschke and Russell, 2010, *J. Cosmol*, 10, 3200; Simoncini et al. *J. Cosmol*, 10, 3325). Inorganic transition metal sulfides could act as precursor catalysts to hydrogenase, nitric oxide reductase, carbon monoxide dehydrogenase and acetyl coenzyme-A synthase, while phosphate could be polymerized to pyrophosphate by protons streaming through the spontaneously precipitated inorganic membrane, in turn condensing and polymerizing the first organic products of hydrogenation and amination. Resulting highly flexible uncoded and heterochiral peptides could locally also lower entropy by sequestering inorganic sulfide and phosphate clusters, thereby improving and tuning their catalytic and energy-storage propensities. Thus, such a system would already be capable of evolution through the survival of those peptides that nested or otherwise interacted with the inorganic entities within the compartments (Milner-White and Russell, 2010, *J. Cosmol*, 10, 3217; Kurland, 2010, *Bioessays* 32, 866). Products not taking part in further interactions would tend to be entrained in the slowly diffusing effluent and be lost to the system. In further conceptual steps Dieter Braun and collaborators (e.g., Baaske et al., 2007 *PNAS*, 104, 9346) have demonstrated how convectively-driven polymerase chain reactions whereby DNA molecules that are replicated, albeit with the involvement of *taq* polymerase, are concentrated against entropy in “cold traps” within inorganic compartments through thermal diffusion driven by thermal gradients acting across the margins of a hydrothermal mound. We know entropy traps are also required for the onset of the RNA world. For example, Sievers et al. (2004, *PNAS*, 101, 7897) show that the peptide bonding rapidly effected in the ribosome is mainly a result of juxtaposing the substrates—perhaps aided by an unfolded peptide—to the partial exclusion water (and see Hsiao et al., 2009, *Nucl Acids Res*, 37, 3134; Wallin and Åqvist, 2010, *PNAS*, 107, 1888).

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THE CONTRIBUTION OF SELF-ASSEMBLING SYSTEMS IN THE STUDY OF LIFE ORIGIN

Dr Sandra Ristori

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In this talk the main issues concerning the role that self-assembly might have played in the emergence of the earliest life forms will be briefly outlined, with special focus on the thermodynamics of restricted systems and on the importance of building up membranes with high resistance to hostile environments. The milestone work in this field carried out by the research groups of Pier Luigi Luisi (on vesicles formation)ⁱ and by Ole G. Mouritsen (on the evolution of lipid molecules)ⁱⁱ will be also reviewed. Complementing such key concepts with experimental data obtained by new and powerful techniques can be fruitful for future investigation. These methods include large scale facilities Small Angle Scattering, such as SAXS and SANS, as well as smaller scale laboratory apparatus, such as high sensitivity Isothermal Titration Calorimetry. The combined use of these techniques on model systems will provide a range of new insights on the thermodynamic and structural details of boundary systems (membranes) and on the occurrence of processes (metabolism, signalling), which are fundamental to the onset of protocells.

In the context of this field of investigation the wide expertise acquired by the research teams of interuniversity centres, such as Center for Colloid and Surface Science (Consorzio Interuniversitario per lo Sviluppo dei Sistemi a Grande Interfase, CSGIⁱⁱⁱ) in Italy, can be a valuable tool to transfer methodological approaches from actual biologically and technologically relevant systems to models for the study of life's origin.

Following the fate of Acetate: Validating Biosignatures for In Situ Planetary Exploration.

Laurie Barge

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We propose a study of the effects of intense radiation environments on molecules relevant to life (such as acetate) to better constrain *in situ* life detection. A problem with detection of biosignatures during space exploration of planetary surfaces is the high probability that organic molecules would be degraded and/or destroyed by highly oxidizing conditions, high-UV surface radiation and charged particle irradiation processes. Furthermore, there is the possibility that organic molecules could be generated via photolysis or other abiotic energy sources, and it may be difficult to distinguish between biological and abiological origins. It is therefore necessary to validate certain molecules which show such duality so that the potential for habitability or possible presence of past life can be accurately assessed with instruments on future space landers and by remote observations. This study will investigate 1) the abiotic formation of organic molecules that may be mistaken for biosignatures; 2) the retention and detection of organics in chemical precipitates relevant to the emergence of life; and 3) the degradation of organics in harsh radiation environments and detection/identification of products. We choose to first focus on acetate (CH_3COO^-) as a possible biological molecular fingerprint since acetogenesis is the simplest and most primitive known metabolism on Earth, and in an alkaline hydrothermal emergence of life scenario, acetate may be one of the first organics formed that could indicate the presence of life. Acetate is also a waste product of other common metabolic pathways, such as sulfate reduction, and could serve as an indicator of extant life. We will also initially focus on environments/chemical conditions relevant to a hydrothermal origin of life hypothesis on Mars, since current landing site choices for the upcoming Mars Science Laboratory mission may have once hosted hydrothermal activity, and so this work will be of immediate relevance to NAI's goals and could provide new significant data for the exploration of Mars.

Molecular self-assembly on surfaces

E. Mateo-Martí

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The aim of the present research is to study the interaction of biomolecules, among them single amino acids, on metallic and mineral surfaces, and their chemical reactivity by means of powerful surface science techniques. Therefore, the use of simple biomolecules gives fundamental and significant information, including an adequate control of biomolecule-surface interactions, which would not be possible with more complex molecules. Furthermore, these studies are focussed on the catalytic properties of different surfaces that could be involved in the formation of prebiotic organic compounds.

These studies have been developed under ultra high vacuum (UHV) clean environment working conditions, therefore, it will be possible to use several complementary *in-situ* surface science techniques such as X-ray photoemission spectroscopy (XPS), infrared spectroscopy (RAIRS), scanning tunnelling microscopy (STM), low energy electron diffraction (LEED) and temperature programmed desorption (TPD) for the characterization of molecular interactions on surfaces. By the complementary use of several techniques we will obtain models of molecule-surface adsorption, which will include information about the self-assembly of biomolecules on surfaces, the chemical state of the adsorbates and therefrom, atomic models to improve our understanding of molecular self-ordering processes.

RNA world and evolution of replicators

Sergio Branciamore¹, Walter de Back², Enzo Gallori¹

¹*Department of Physics and Astronomy University of Florence, Largo E. Fermi 2, 50125 Florence, Italy,* ²*Center for High Performance Computing (ZIH), Dresden University of Technology, Germany*

Manfred Eigen in his seminal work pointed out the difficulties inherent in increasing information in a system of replicators. Since then many different *ecological solutions* have been proposed in order to overcome the Eigen paradox: “no enzyme without genome no genome without enzyme”. The basic idea was that different replicators interact in a cooperative fashion such that selection operates not at the level of the single replicator but at the level of the cooperating ensemble. However if and how this cooperation could emerge still remains a mystery. It was pointed out that the evolutionary tendency of replicating molecules is to optimize their own replication capacity rather than cooperate with other replicators as in the *in vitro* evolution experiments of Spiegelman. Here, we investigate the evolution of a metabolic system, starting from a population of noncatalytic RNA. Our simulations suggest a possible route towards the evolution of template cooperation and coexistence in an RNA world.

Populations of RNA Molecules as Computational Model for Evolution

Michael Stich

*Dpto de Evolución Molecular, Centro de Astrobiología (CSIC-INTA),
Ctra de Ajalvir, km 4, 28850 Torrejón de Ardoz (Madrid), Spain*

We consider populations of RNA molecules as a computational model for molecular evolution. In the first place, we study the sequence' structure map, its implications on the structural repertoire of a pool of random RNA sequences and its relevance for the RNA world hypothesis of the origin of life. In a scenario where template replication is possible, we discuss the internal organization of evolving populations and its relationship with robustness and adaptability. Finally, we explore how the effect of the mutation rate on fitness changes depends on the degree of adaptation of an RNA population.

Dust driven complexity and preservation of organics

John Robert Brucato

Department of Physics and Astronomy University of Florence, Largo E. Fermi 2, 50125 Florence, Italy

Silicates could have played an important role in driving the formation of complex molecular compounds relevant for prebiotic chemistry. Due to the low efficiency of formation of complex molecules in the gas phase, in fact, it is not feasible for an active gas-phase chemistry to take place at low temperatures with condensate molecules strictly in contact with dust. Laboratory experiments have shown that different chemical-physical mechanisms might be responsible for the richness of molecules observed in space. Surface catalysis at low temperature by dust is considered necessary to justify the presence of, e.g., H₂, H₂O or CO₂, as demonstrated experimentally according to the Langmuir-Hinshelwood mechanism. To describe the presence of more complex molecules, such as CH₃OH, or radicals and even organic refractory material, irradiation processes due to ions and UV photons are required. Therefore, chemical compounds synthesized in the presence of dust grains may become even more complex in high-energy environments or if such materials are combined with fluids such as might exist in the interior of a carbon-rich asteroid.

Prebiotic reactions have thus been studied in the laboratory in conditions simulating the environments found on the early Earth and in space. Silicate cosmic dust analogues were used as catalysts, in particular olivine (Mg,Fe)₂SiO₄. This is because olivine is continuously confirmed by observations to be ubiquitous in space. The chemistry studied was that of formamide (NH₂COH). This very simple molecule, containing only one carbon atom, was observed to be present in different space environments, as gas in the interstellar medium or in the long period comet Hale-Bopp and in the solid phase on grains around the young stellar object W33A. Formamide is a promising route to understand the first chemical steps that brought simple C-bearing molecules towards largely complex mixtures of bio-macro-molecules.

The effect of inorganic catalysts on the prebiotic chemistry of formamide has been extensively studied showing that the selectivity of the transformation is correlated to chemical properties and elemental composition of the catalyst. Our findings suggest that the synthesis of six intermediates of the citric acid cycle can be performed from formamide and TiO₂ under simple photochemical conditions that are, in principle, plausible with a prebiotic scenario. From a Darwinian point of view the citric acid cycle is postulated to have evolved by combination of several pre-existing enzymes from pathways for biosynthesis of aspartate and glutamate. The origins of this cycle may be found in the more primitive anaerobic organisms of the past where minerals might play the role of ancestor of enzymes (Szostak et al., 2001).

This predisposition would have allowed the synthesis of metabolic or genetic compounds to operate on the early Earth or in space under geo- and cosmo-chemical conditions specific for each assembly sequence. These data, together with a collective study of various atmosphere and surfaces in the Solar System, would lead to an understanding on common processes that may be active on all planets, such as heterogeneous

photocatalysis, also providing clues on the initial phases when life emerged that are not preserved on Earth.

Stability and disorder in genome evolution

Francisco J. López de Saro

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Ctra de Ajalvir, km 4, 28850 Torrejón de Ardoz (Madrid), Spain*

All living organisms have their genetic information organized in the form of genomes. An often-overlooked fact in the history of life is that the basic design of prokaryotic (bacterial) genomes has probably remained unchanged for 3.8 billion years. Genomes are therefore a form of information organization that allows evolution and adaptation despite high architectural uniformity. I am interested in understanding the driving forces of genome organization, structure, and evolution. In the last decade a large amount of information on the genomes of all living organisms has been obtained, which allow for some generalizations about how genetic information evolves and is disseminated. Therefore, by analyzing what are the basic rules that govern genome structure it may be possible to understand how they originated and what are the keys to their stability and robustness.

Beyond Thermodynamic Cycles: A Simple Model of Metabolic Closure

Gabriel Piedrafita

Dept. Biochemistry and Molecular Biology, University Complutense of Madrid, Spain.

From a thermodynamic point of view, the emergence of life could be considered a process of self-organization. Nevertheless, some theories of life claim that living entities should indeed be distinguished by a common basic organization, beyond self-organization, based on the fact that living organisms must not only organize themselves from within; they must also maintain their organization in the face of changes in its environment and continuous degradation of their components, highlighting the need of active molecular mechanisms (self-construction) to achieve self-maintenance. In this sense, the theory of (M,R)-systems or *metabolism-repair systems* [1] perhaps comes closer to a complete explanation of life, facing the problem of *closure to efficient causation*, i.e. the necessity for all of the catalysts essential for survival of an organism to be produced internally, as an organism cannot rely on any external agent for maintaining it. But unfortunately it was explained in abstract terms, devoid of any biological example or model that would relate it to any ordinary ideas of biochemistry.

To give concrete expression of the idea of an (M,R)-system, we have recently proposed a simple model [2] (Fig 1A) consisting of three intertwined catalytic cycles that are together capable of producing their own catalysts. The dynamic analysis reveals that it can establish a non-trivial steady state and maintain it by replenishing the catalysts despite their continuous loss by irreversible degradation. It can also construct itself by “seeding” it with a sufficient quantity of at least one of the catalysts needed for functioning. The system shows bistability (Fig 1B), because too restrictive initial concentrations are insufficient to reach the non-trivial steady state and leads to collapse, a trivial steady state. Once formed, it is robust, being capable of withstanding long perturbations in the concentrations of most of its components.

Regardless of the controversy of whether a whole organism can be simulated or not, this model shows the feasibility of simulating the behaviour of a system that is closed to efficient causation, contributing to the clarification of some ideas of the theory of (M,R)-systems. Moreover, the simplicity of this robust self-maintaining system and its capacity to be easily seeded may allow us to regard it as a plausible model of a prebiotic system.

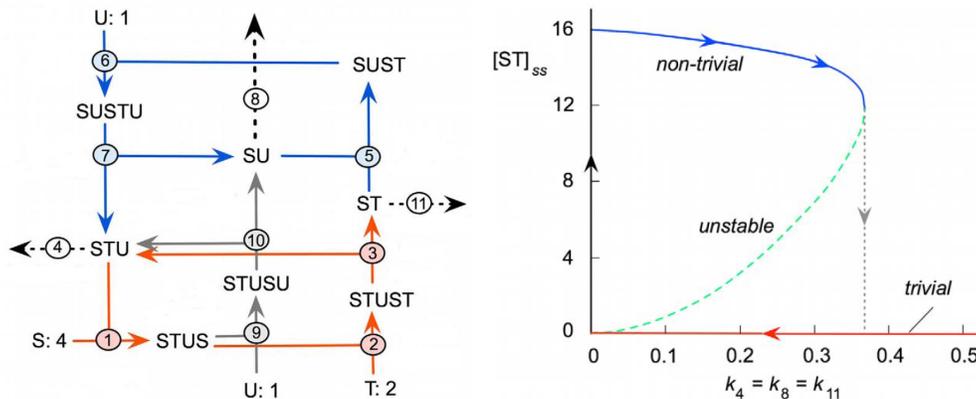


Fig. 1. (A) A simple kinetic model of an (M,R)-system. The three interlocked cycles (in different colours) produce their own catalysts STU, SU and ST. (B) Bifurcation diagram showing the wide bistability region found with relatively small degradation rate constants.

References

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2. Piedrafita, G., Montero, F., Morán, F., et al. (2010). A simple self-maintaining metabolic system: robustness, autocatalysis, bistability. *PLoS Comput Biol*, 6(8): e1000872. doi:10.1371/journal.pcbi.1000872.

Optimum mutation rates in the framework of the Manfred Eigen's quasispecies model

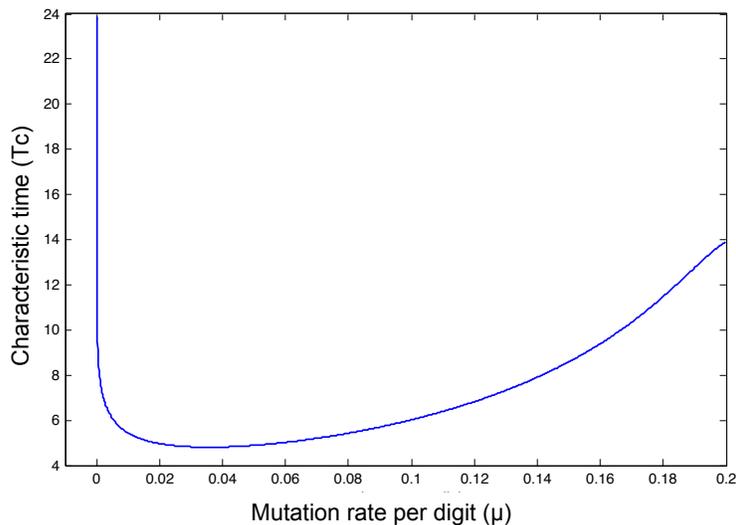
Arturo Marín Alguacil

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The time that an error-prone self-replicative system takes to go from one quasispecies to another with higher selective value must depend on the mutation rate. In fact, some previous results obtained from stochastic models in which the evolution time is quantified by measuring the time when the target sequence shows up for the first time in the population, have demonstrated that optimal mutation rate exists [1]. How to measure time in a deterministic system? To measure the time implies imposing more fitness sequence, so we used a methodology based on transition times (Characteristic time) [2], which is defined by this equation:

$$T_c = \frac{\int_0^{\infty} t \frac{dx}{dt} dt}{\int_0^{\infty} \frac{dx}{dt}} \Rightarrow \frac{A}{h}$$

The aim of this communication is to explore, from a quantitative point of view, the dependence of the optimal evolutionary time on the different parameters of the system such as the shape and other properties of fitness landscape. At this end, deterministic models in the framework of those proposed by Eigen [3] have been developed, and in all the cases an average evolutionary time has been evaluated as previously described [2]. In two peaks fitness landscape and rugged fitness landscape the optimum mutation rate (minimum T_c) has been found. Optimum mutation rate in two peaks fitness landscape:



Detection of parameters related to the life cycle on planetary atmospheres

Manuel de la Torre Juárez

Jet Propulsion Laboratory, Pasadena, CA

All known planetary atmospheres are highly turbulent. As a consequence, probability distribution functions (PDFs) of magnitudes such as velocity, temperature, moisture change with location. Taking the Earth as an example, it is shown that when one observes its cloud properties relevant for its radiative cycle, different spatial resolutions result in different PDFs of those cloud properties. It is shown that these PDFs are different for each property and all change with scale following different laws. As a consequence, when averaging over all these distributions, mean values and standard deviations change with the resolution of the observation. Low spatial resolution observations of exoplanetary atmospheres are thus equally subject to a bias and one might be attributing to an exoplanet chemical abundances that are either overestimates or underestimate depending on the sign of the asymmetry in their probability distribution function. It is found also that, at least on Earth, there may be a universal common description when one quantifies the PDFs of the mean value inside each resolved pixel and its standard deviation, that the scaling is consistent with turbulent scaling and the shape of at least one variable (cloud particle size) is consistent with entropy maximization model predictions, thus providing a possible parameterization to characterize partially the statistics at sub-pixel resolutions.

Theoretical aspects of the effects of life in planetary atmospheres

Alfonso Delgado Bonal

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It is well known that every live system is in a disequilibrium state, in the sense of thermodynamical description. Some work has been done in an attempt to understand those states and provide to them a thermodynamical description with fixed variables, as Energy, Entropy or Gibbs Energy. However, that work is done today with a huge mathematical effort, due to the complication of the formulation. Thermodynamics, unlike other branches of physics, is completely phenomenological, not based in “first principles” like Particle physics or the Gravitation theory. If we want to reduce the theory to that, we have to consider some inherent complications of the theory, such the inability to measure the entropy in a system, and, in live systems, the disequilibrium complications.

Those problems lead us to try to explain thermodynamics as a Lagrangian system, where the mathematics are better known and where the constraints like disequilibrium or biosphere could be easily added. This is not the first time that the physicist wants to study this branch in this way (see for example L. D. Landáu, E. M. Lifshitz, *Course of Theoretical Physics*, Vol. 5 and Vol. 9 (Statistical Physics)), but is the first time that the Lagrangian formalism is being used to study a dynamical system in disequilibrium like a planetary atmosphere.

Also, the Lagrangian formalism has the time variable included in the formulation, so the evolution of a system is nothing more than a dimensional feature of itself, that lead us to study the atmosphere evolution in an easy way.

Evolution of Earth transmission spectra and effects on the emergence of life

Jorge Pla García

Ctra de Ajalvir, km 4, 28850 Torrejón de Ardoz (Madrid), Spain Centro de Astrobiología (CSIC-INTA)

I will develop a characterization of the evolution of Earth's atmosphere in order to model the observable spectra of an Earth-like planet through its history. These calculations are designed to guide the interpretation of an observed transmission spectrum of such a planet by future instruments, like TPF or Darwin, that will characterize exoplanets.

I will focus on planetary environmental characteristics whose resultant spectral features (**biomarkers**) can be used to imply habitability or presence of life and the disequilibrium that causes **this** in the atmosphere. These features are generated by H_2O , CO_2 , CH_4 , O_2 , O_3 , N_2O , and vegetation-like surface albedos.

I will use a combination of FUTBOLIN (thermal IR) and VLIDORT (thermal IR and scattering) radiative transfer models to run the Early Earth Kasting models in order to obtain such synthetic transmission spectra and then compare with current Earth transmission spectra measurements from earthshine observations (light reflected from the Moon towards the Earth during a lunar eclipse).

During a planetary transit, the planet passes in front of the star and occults the stellar flux in the amount equal to the ratio of the planet-to-star area. During the transit, some of the stellar flux pass through the optically thin part of the planet atmosphere, the part of the atmosphere above the planet limb, and in a few cases the basic atmospheric **composition can** be estimated. Some biologically relevant atmospheric features that are weak in the reflection spectrum, such as ozone, molecular oxygen, water, carbon dioxide and methane **are much stronger** in the transmission spectrum, and indeed stronger than predicted by modelling.

DISCUSSION

The last day of the Workshop was dedicated to propose, and discuss, a list of ideas that could lead to potential proposals either in USA or Europe or both. For each idea we compiled a list of positive and negative comments. This is the list of proposed ideas. Due to sensitive content, the summary and discussion will be distributed as an internal document within the members of the TDE Focus Group.

List of ideas:

- Radiation of acetate.
- Pyrophosphate Generation Via an Ambient Proton-Motive Force?
- Pattern forming / self-organising membranes.
- Proton gradient energy. Abiotic anti-entropy synthesis.
- Detailing how a proton gradient across an inorganic membrane might drive pyrophosphate formation
- Thermodynamic processes in Martian environments and habitability.
- Quantify and constrain disequilibrium due to abiotic/biotic processes.
- How can thermodynamics help define life as it could be?
- Bridging the metabolic to information gap.
- Thermodynamic Earth system function
- Can turbulent scaling help justify MEP for macro scale processes?
- Spectral measures/signals/indicators of MEP.
- Tectonic perpetration of serpentinization fracture-engines empowered the production and reproduction of the first metabolic engines?

Next Workshop: Second week of September in Florence, Italy